Making fate and exposure models for freshwater ecotoxicity in life cycle assessment suitable for organic acids and bases

- Supporting Information -

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Model adaptations

Ionizing chemicals can dissociate in water. Water is present in soil and sediment and it occurs as aerosol and cloud water in the air compartment. The degree of speciation can be determined in each compartment with use of the acid dissociation constant (pKa) of the chemical and the pH of the water phase of the environmental compartment. The fraction of neutral species (F_n) and the fraction of ionic species (F_i) were determined with the Henderson-Hasselbalch equation (Henderson, 1908):

$$F_n = \frac{1}{1 + 10^{a(pH - pK_a)}} \quad \text{(A1)}$$

$$F_i = 1 - F_n \quad \text{(A2)}$$

where a is 1 for monovalent acids and -1 for monovalent bases. Table A1 shows the compartments included in USES-LCA 2.0 (Van Zelm et al., 2009) and the pH values that were ascribed to the various water phases (Stumm and Morgan, 1981; Delle Site, 2001; Armitage et al., 2009).

Table A1: The various environmental compartments and the pH of the water phase (Stumm and Morgan, 1981; Delle Site, 2001; Armitage et al., 2009).

compartment	pH water phase
air - cloud	5.6
air - aerosol	3
natural soil	5

agricultural soil	7
other soil	7
freshwater	7
freshwater sediment	7
seawater	8
seawater sediment	8

Aerosol and cloud water

Aerosol particles in air and water in clouds were included in the adapted model of USES-LCA 2.0 to represent the humidity in air. An aerosol content in air of $2 \cdot 10^{-11}$ m^3/m^3 with an organic carbon content of 0.1 g/g were obtained from Franco and Trapp (2010).

Partition coefficients

Air-water

For the ionized fraction of the acid or base, the air-water partition coefficient is set to zero. Ions have no measurable vapor pressure and therefore do not volatilize.

Solid-water

Solids are present in atmosphere (in aerosol), water (as suspended matter), soil and sediment. The soil-water partition coefficient normalized to organic carbon (Koc) is used to determine the partitioning of chemicals (K_d) between the solid and water phase of a compartment. The regressions for the Koc were expanded by regressions that are optimized for acids and bases (Franco et al., 2009). Equation A3 shows the calculation of the dimensionless solid-water sorption coefficient from the K_{OC}. Equations A4 and A5 show the regressions for the K_{OC}.

$$K_d = K_{OC} * f_{OC} * \rho_S \quad \text{(A3)}$$

Acids: $K_{OC} = \phi_{nS} * 10^{0.54 \cdot logK_{OW} + 1.11} + \phi_{-s} * 10^{0.11 \cdot logK_{OW} + 1.54}$ (A4)

Bases: $K_{OC} = \phi_{nS} * 10^{0.37 \cdot logK_{OW} + 1.70} + \phi_{+s} * 10^{pKa^{0.65} \cdot f^{0.14}}$ (A5)

Where

f_{OC} = organic carbon content of the dry matter (g/g)

ρ_S = density of the solids (kg/L)

Φ_{nS} = neutral fraction

Φ_{-S} = ionized fraction (acids)

Φ_{+S} = ionized fraction (bases)

K_{OW} = octanol-water partition coefficient of the neutral compound

pKa = acid dissociation constant

f = diffusion limiting factor, described by $K_{OW\_7}/(K_{OW\_7}+1)$, with Kow_7 being the apparent Kow at environmental pH of 7

aerosol-air

Aerosol particles in air consist of a water and a solid phase. The neutral fraction of a chemical can enter both the water and solid phase from the gas phase of the air compartment. In the water phase of aerosol, ionization can take place and the ionized fraction can partition to the solid phase of aerosol. Partitioning from the gas phase into aerosol water is calculated using the air-water partition coefficient of the neutral species, Kaw, correcting for the fraction in the neutral form:

$$K_{aerw} = \frac{C_{aer}}{C_{gas}} = \frac{1}{K_{aw} \cdot \Phi_{n,S}} \quad \text{(A6)}$$

Partitioning from the gas phase into aerosol solids is calculated according to the Bidleman equation (Harner and Bidleman, 1998), adjusted according to Götz et al. (2007).

$$K_{p,dry} = \frac{C_{aer}}{C_{gas}} = 0.54 \cdot \frac{K_{ow}}{K_h} \cdot \mathrm{CORG}_{\mathrm{aer}} \cdot \frac{\rho_{\mathrm{aers}}}{1000} \qquad \text{(A7)}$$

Acids and bases included

All acids and bases with their CAS numbers, log Kow, pKa and old and new fate factors and exposure factors are in a separate excel file (Appendix B).

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